3. A formula for the determination of the apparent activation energy of the electrochemical process at a rotating-disc electrode has been obtained on the basis of the above relationship.

1. S. V. Gorbachev, Zhur. Fiz. Khim., 26, 1303 (1952).
2. V. G. Levich, "Fiziko-Khimicheskaya Gidrodinamika" (Physicochemical Hydrodynamics), Izd. Akad. Nauk SSSR, 1952.
3. N. A. Izgaryshev and S. V. Gorbachev "Kurs Teoreticheskoi Elektrokhimii" (A Course of Theoretical Electrochemistry), Goskhimizdat, 1951; A. N. Frumkin *et al.*, "Kinetika Elektrodnykh Protsessov" (Kinetics of Electrode Processes), Izd. Moskov. Univ., 1952.
4. Karman, Z. angew. Math. Mech., 1, 235 (1921); W. Cochran, Proc. Cambridge Phil. Soc., 30, 365 (1934).
5. M. Sand, Phil. Mag., 1, 48 (1901); Weber, Wied. Ann., 7, 536 (1879); Karaoglanoff, Z. Elektrochem., 12, 5 (1906); S. V. Gorbachev, Zhur. Fiz. Khim., 30, 1484 (1956).

Mendeleev Institute of Chemical Technology, Moscow

Received 3rd December 1959.

HYDROGEN OVERVOLTAGE AT A ZINC ELECTRODE IN ALKALINE SOLUTIONS. EFFECT OF POTASSIUM HYDROXIDE CONCENTRATION†

Z. A. Iofa, L. V. Komlev, and V. S. Bagotskii

The aim of this work was to measure the hydrogen overvoltage at a clean zinc electrode in alkaline solutions, as used in chemical primary cells. It was also desired to establish some general characteristics of the kinetics of hydrogen evolution from solid metals of high overvoltage in alkaline solutions.

Polinskii[1] has carried out careful measurements of the hydrogen overvoltage on zinc in acid solutions. Using single-crystal, spectroscopically pure (twice vacuum-distilled) zinc in $1N\ H_2SO_4$ at 25°, he obtained $\eta = 1.24 + 0.118 \log i$ for the overvoltage, where i is current density in A cm^{-2}. Rotinyan, Fedot'ev, and Li Un Sok[2] obtained similar results for zinc in sulphuric acid. There is a lack of reliable data on the hydrogen overvoltage of zinc in alkaline solutions and, in particular, on the effect of alkali concentration on the overvoltage. In alkaline solutions water molecules are reduced[3] at a cathode

$$H_2O + e \rightarrow H_{ads} + OH^-. \qquad (I)$$

Hydrogen evolution as a result of the discharge of free hydronium ions is negligible in alkaline solutions since the rate of dissociation of water molecules and of formation of hydronium ions is very low and quite incapable of giving rise to a sufficient concentration of these ions[4].

The rate of reaction (I) is given[1] by the equation

$$i = k c_{H_2O} \exp\left[-\frac{\alpha F(\varphi - \psi_1)}{RT}\right], \qquad (1)$$

whence the electrode potential is

$$\varphi = \text{const} + \psi_1 + \frac{RT}{\alpha F} \ln c_{H_2O} - \frac{RT}{\alpha F} \ln i. \qquad (2)$$

In dilute solutions of pure alkalis (free from other electrolytes) the variation of ψ_1 with c_{KOH} is given by the elementary theory of the structure of the diffuse double layer in the form

$$\psi_1 = \text{const} + \frac{RT}{F} \ln c_{KOH}, \qquad (3)$$

whence the electrode potential can be expected to change towards more positive values when the alkali concentration is increased:

$$\varphi = \text{const} + \frac{RT}{\alpha F} \ln c_{H_2O} + \frac{RT}{F} \ln c_{KOH} - \frac{RT}{F} \ln i. \qquad (4)$$

In concentrated solutions of alkalis, or in solutions in which the ionic concentration is kept constant by adding auxiliary electrolytes the value of ψ_1 may be taken as constant to a first approximation. In this case the potential at which hydrogen is evolved is independent of the pH of the solution,

$$\varphi = \text{const} + \frac{RT}{\alpha F} \ln c_{H_2O} - \frac{RT}{\alpha F} \ln i, \qquad (5)$$

and only at very high concentrations can a slight variation be expected, due to the change in concentration of water molecules.

If we now consider the expression for the overvoltage, $\eta = \varphi_e - \varphi$, where φ_e is the equilibrium potential of the hydrogen electrode in alkaline solutions at constant p_{H_2}, given by

$$\varphi_e = \text{const} + \frac{RT}{F} \ln \frac{a_{H_2O}}{a_{OH^-}}, \qquad (6)$$

we obtain

$$\eta = \text{const} - \psi_1 - \left(\frac{1-\alpha}{\alpha}\right)\frac{RT}{F} \ln a_{H_2O} - \frac{RT}{F} \ln a_{OH^-} + \frac{RT}{\alpha F} \ln i \qquad (7)$$

for the general case,

$$\eta = \text{const} - \left(\frac{1-\alpha}{\alpha}\right)\frac{RT}{F} \ln a_{H_2O} - \frac{2RT}{F} \ln a_{OH^-} + \frac{RT}{\alpha F} \ln i \qquad (8)$$

for pure, dilute solutions of alkali [adopting Eqn. (3)], and

$$\eta = \text{const} - \left(\frac{1-\alpha}{\alpha}\right)\frac{RT}{F} \ln a_{H_2O} - \frac{RT}{F} \ln a_{OH^-} + \frac{RT}{\alpha F} \ln i \qquad (9)$$

for concentrated solutions of alkalis.

The derivation of all these relationships involves a number of simplifying assumptions. Thus, the concentration of water in the rate equation (2) (conceptually, this is the concentration in the layer of solution adjacent to the electrode) is identified with the water activity in the thermodynamic equation (6), c_{KOH} is identified with a_{OH^-} in Eqns. (3) and (6), and so on.

The predictions of the slow-discharge theory, expressed by the above equations, regarding the dependence of hydrogen overvoltage on pH in alkaline solutions have not yet been tested over a wide range of alkali concentrations.

† The experimental part of this investigation was carried out with the assistance of E. I. Mikhailova.

EXPERIMENTAL

The solutions, made from chemically pure KOH and doubly distilled water, were purified by protracted (7–10 days) cathodic treatment in a polystyrene cell, with a zinc cathode operated at a current density of at least 50 mA cm^{-2}. The cathode was cleaned every day by scraping the contaminated surface with the sharp edge of a piece of glass‡. Deposited impurities could be seen, initially, as a dark film, but after a few days the electrode remained bright and clean. In a few experiments, twice recrystallised KOH was used, prepared in an apparatus similar to that described by Bokris and coworkers[5]. Solutions prepared from this material needed to be cathodised for a shorter time than had normally been found necessary to give reproducible overvoltage values, and did not produce dark deposits on the cathodes. The experimental cathode was prepared from spectroscopically pure zinc. It was subjected to 30 min preliminary cathodic polarisation at high current density in the experimental cell. The polarisation curve was explored in both directions during 2–4 h, until reproducible results could be obtained.

The polarisation was measured by the conventional compensation method at 20° with respect to a hydrogen electrode immersed in the same alkaline solution, but in the case of concentrated solutions above 7*N* a mercuric oxide electrode was used, also immersed in the same solution. The additive constant for converting from hydrogen to mercuric oxide reference electrodes was checked for each solution.

Several experiments were carried out at each alkali concentration. The scatter of overvoltage values was not more than 5 mV in any one experiment; among independent experiments, the scatter amounted to 10 mV. The values reported below are averages.

Fig. 1 shows the variation of η with $\log i$, measured in 0.1, 0.2, 1, 5, 7, and 10*N* KOH solutions, and Fig. 2 gives the results obtained with 10, 13, and 14 *N* KOH. It can be seen that the variation of η with $\log i$ remains linear from about 10^{-5} to 5×10^{-2} A cm^{-2}. The constants in the equation $\eta = a + b \log i$ for these solutions are set out in the Table as well as the mean ionic activities $a_{\pm}$ and the activities of water molecules a_{H_2O} in KOH solutions taken from the literature[6].

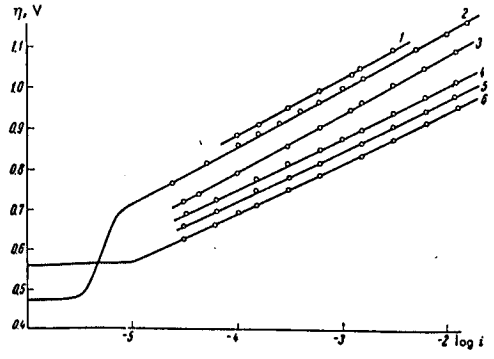


Fig. 1. Variation of hydrogen overvoltage with the logarithm of current density in KOH solutions from 0.1 to 10 *N*: 1) 0.1; 2) 0.2; 3) 1; 4) 5; 5) 7; 6) 10 *N*.

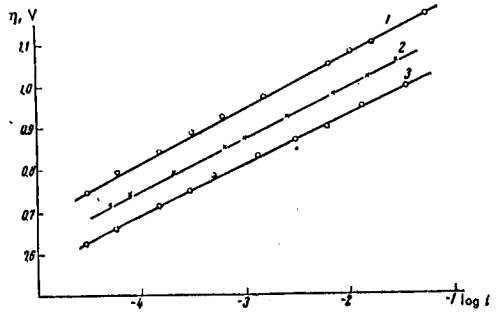


Fig. 2. Variation of hydrogen overvoltage with the logarithm of current density in KOH solutions from 10 to 14*N*:
1) 14; 2) 13; 3) 10 *N*.

TABLE.

c, N	0.1	0.2	1	5	7	10	13	14
b	0.128	0.130	0.130	0.120	0.118	0.118	0.120	0.125
a	1.394	1.375	1.312	1.230	1.189	1.164	1.230	1.235
$\log a_{\pm}$	−1.202	−0.818	−0.122	0.957	1.470	2.05	2.644	2.841
$\log a_{H_2O}$	0.00	−0.01	−0.02	−0.11	−0.18	−0.40	−0.75	−0.96

On decreasing i and approaching the steady-state potential, a sharp decrease in overvoltage was observed with solutions of relatively low KOH concentration. At high concentrations the drop was smaller or even completely absent. This is illustrated by the curves of Fig. 1 referring to 0.2 and 10*N* KOH. For the remaining KOH concentrations, the low current density region is not given in the figures as it lacked reproducibility.

The overvoltage values of Figs. 1 and 2 and of the Table refer to current densities calculated per cm^2 of apparent surface of the zinc cathode, which was quite smooth, and possibly 1.5–2 times smaller than the true surface area. The overvoltage values will thus be increased by 20–30 mV if recalculated for true surface areas.

‡ In a few experiments the solution was purified on mercury with a cathodic polarising current of $\sim 10^{-5}$ A cm^{-2}.

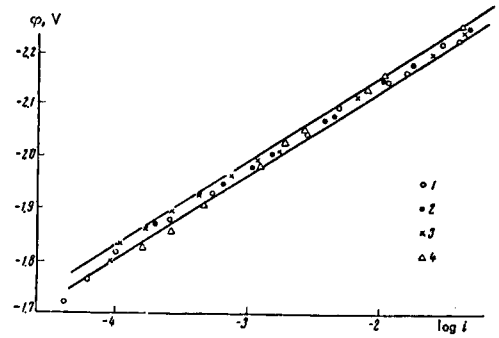


Fig. 3. Variation of hydrogen overvoltage with the logarithm of current density in solutions of composition c_1 KOH + c_2 KCl, where $c_1 + c_2 = 3N$: 1) 3 N KOH; 2) 1 N KOH + 2 N KCl; 3) 0.1 N KOH + 2.9 N KCl; 4) 0.01 N KOH + 2.99 N KCl.

In a separate series of experiments the hydrogen overvoltage was measured at a zinc electrode immersed in solutions of constant total electrolyte concentration but different alkali concentrations. The composition of these solutions was c_1 KOH + c_2 KCl, such that $c_1 + c_2 = 3N$. The KOH concentration was varied from 0.01 to $3N$. The results of this work, presented in Fig. 3, show that if the ionic strength of the solution is kept constant whilst the KOH concentration is varied the electrode potential (not the overpotential) remains constant within the limits of uncertainty of the measurement for i = const.

DISCUSSION

The variation of the overvoltage of a zinc electrode in alkaline solutions with the logarithm of the current density gives a slope b = 0.12 V; a value of 0.5 for the constant α in the rate equation (1) is thus indicated.' This value agrees with the results of measurements in acid solutions and thus provides evidence that an electric field has similar effects on the rates of electron-transfer reactions involving H_3O^+ and H_2O. The somewhat higher value found for the b slope in dilute solutions is probably due to a residual oxide layer on the electrode surface.

When the data given in the Table are compared with the hydrogen overvoltage values reported for zinc in acid solutions, the constant a in 1N alkali is found to be about 0.08 V higher than the corresponding value for a sulphuric acid solution of the same concentration. The similarity between the values of this constant in acid and in alkaline solutions of the same concentration is a consequence of the kinetic law described by Brönsted's well-known equation[7].

Fig. 4 shows the variation of the overvoltage at a current density of 10^{-3} A cm^{-2} with the logarithm of the mean ionic activity, $a_\pm$, of the KOH solutions. The curve goes through a minimum at $c_{KOH} \sim 9-10N$.

The results presented in Figs. 3 and 4 show that in not too concentrated alkali solutions the main predictions of the slow-discharge theory are verified. In solutions of constant electrolyte concentration (Fig. 3), and also in solutions of intermediate KOH concentration (from 1 to 7N, Fig. 4), in which ψ_1 can be taken to be approximately constant, the overvoltage decreases by about 0.06 V when the pH is increased by one unit, or, in other words, the potential of the polarised electrode is independent of pH. In more dilute solutions the overvoltage becomes more sensitive to pH, the slope increasing to 0.09–0.10 V. This is close to the limiting value of 0.12 V, derived by applying the laws of dilute solutions to the change in ψ_1 potential.

In concentrated solutions there are appreciable deviations from the above pH dependence of the overvoltage. The overvoltage shows a sharp increase at KOH concentrations 10–14N, amounting to about 0.16 V. But according to Eqn. (9) the change in activity ($a_\pm$) should lower the overvoltage by 46 mV for this increase in concentration. At these concentrations we may already be observing the effect of changes in the activity of the water, which will increase somewhat the overvoltage since the activity must decrease with increasing concentration of alkali. However, the tabulated data for the activity of water predict an increase in overvoltage of only 30 mV *i.e.* they cannot even completely compensate the decrease in overvoltage due to the increase in the activity of alkali. We are thus unable to explain by these considerations alone the fact that $(\partial\eta/\partial \log a_\pm)$ falls to zero and even changes sign at KOH concentrations above 10N.

The deviation of the experimental results from the predictions of Eqn. (9), observed in concentrated solutions, is connected, on the one hand, with the above-mentioned simplifying assumptions, which were made in the derivation of this equation and which are generally speaking correct only in highly dilute solutions. On the other hand, the possibility that new specific factors not considered in the elementary theory of the structure of the double layer (and able to affect the kinetics of hydrogen evolution) will arise in concentrated alkali solutions cannot be entirely excluded.

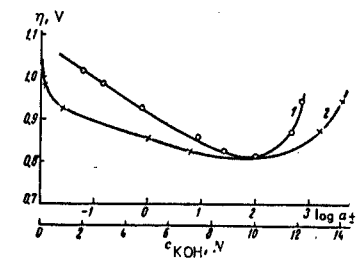


Fig. 4. Variation of hydrogen overvoltage at $i = 10^{-3}$ A cm^{-2} with (1) the logarithm of the mean ionic activity and (2) the concentration of KOH solutions.

In acid solutions the double layer consists of negative charges in the metal and hydrogen ions, on the solution side, held to the metal surface. The electric field of the double layer is confined between the metal and these hydrogen ions, which experience the total effect of the electric field corresponding to the potential in the dense part of the double layer.

In alkaline solutions we find alkali-metal cations on the solution side of the double layer, and the whole of the potential drop in the dense part of the double layer takes place between the metal and the alkali-metal cations, which are not discharged. However, the water molecules which take part in the electrochemical reaction are situated among these cations in the double layer and experience the effect of only part of the lines of force of the field in the double layer. This may be formally allowed for in the rate equations [Eqn. (1), for instance] by subtracting from $(\varphi - \psi_1)$, the total potential drop in the dense part of the double layer, yet another term ψ_i' representing the potential which does not act on the water molecules in the double layer. The larger the absolute value of ψ_i', the higher the overvoltage. The value of ψ_i' can obviously depend on a number of factors, such as the degree of hydration of the alkali-metal cations: the more fully hydrated the cations, the greater the number of water molecules which they will bring into the double layer and the smaller ψ_i'. In dilute solutions of alkali the value of ψ_i' will vary only slightly, if at all, with changes in alkali concentration. In concentrated solutions of alkali a sharp increase in ψ_i' is possible, due both to the decreased hydration of the cations and to the possible changes in orientation of ions and water molecules in the double layer.

The sharp increase in hydrogen overvoltage between 10 and 14*N* KOH is evidence that the screening effect on the water molecules by the alkali-metal cations in the double layer becomes important in concentrated alkali solutions.

SUMMARY

The overvoltage attending the evolution of hydrogen at a clean zinc electrode in KOH solutions from 0.1 to 14*N* has been measured. The semilogarithmic plot of overvoltage against current density is linear, with a slope of about 0.12 V. On increasing the alkali concentration, the overvoltage at constant current density is found to decrease, by 0.09–0.10 V per pH unit in dilute solutions and by about 0.06 V per pH unit in solutions of intermediate concentration. This behaviour agrees with the equations of the slow-discharge theory if account is taken of the effect of the double-layer structure. In concentrated solutions (above 10*N*) the overvoltage increases with pH. This may be due to the increased screening effect of the alkali-metal cations on the water molecules undergoing electron transfer in the double layer.

1. A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, and B. N. Kabanov, "Kinetika Elektrodnykh Protsessov" (The Kinetics of Electrode Processes), Izd. Moskov. Gos. Univ., 1952.
2. A. A. Rotinyan, N. P. Fedot'ev, and Li Un Sok, Zhur. Fiz. Khim., 31, 1295 (1957).
3. P. D. Lukovtsev, S. D. Levin, and A. N. Frumkin, Zhur. Fiz. Khim., 13, 916 (1939).
4. Z. A. Iofa, A. N. Frumkin, and E. A. Maznichenko, Zhur. Fiz. Khim., 31, 2042 (1957).
5. N. Pentland, J. O'M. Bockris, and E. Scheldon, J. Electrochem. Soc., 104, 182 (1957).
6. H. S. Harned and M. A. Cook, J. Amer. Chem. Soc., 59, 496 (1937); B. E. Conway, "Electrochemical Data", 1954.
7. A. N. Frumkin, Z. phys. Chem., 100A, 116 (1932).

Lomonosov Moscow State University

All-Union Research Institute for Current Sources

Received 7th December 1959

ELECTROMOTIVE-FORCE STUDIES OF THE THERMODYNAMICS OF BINARY METALLIC SYSTEMS. VII. IRON–ANTIMONY LIQUID ALLOYS

A. A. Vecher, V. A. Geiderikh, and Ya. I. Gerasimov

In the course of our study of the thermodynamics of the alloys of antimony and iron[1,2] we have investigated the alloys in the liquid state.

EXPERIMENTAL

We have measured the electromotive force of the following galvanic cell:

$$Fe(solid) \mid Fe^{2+}\,(KCl + LiCl\ melt) \mid Fe\text{–}Sb\ (liquid\ alloy).$$

The apparatus (Fig. 1) consisted of a quartz vessel fitted with a ground cap of molybdenum glass, which carried the

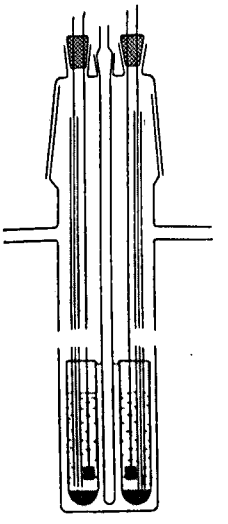


Fig. 1. Experimental assembly.